Chapter

Management of Coal Fly Ash in Remediation Process

Markandeya, S.P. Shukla and Devendra Mohan

Abstract

The present research relates to class of adsorbents obtained by systematic biopolymer modification of cenospheres transfigured from coal fly ash (CFA): an immense waste by-product of coal based thermal power plant, method of preparation thereof and their use in wastewater treatment contaminated by tanneries, distilleries, cosmetics, textiles, plastics, pulp and paper industries, paints, electroplating and food processing industries effluents. Removal percentage of disperse dyes had better correlated with Langmuir isotherm, tested among Freundlich, Temkin and Redlich-Peterson isotherm which indicated saturated monolayer attachment of dye molecules onto the surface of adsorbent with maximum capacity 500.4 and 500.0 mg/g for Disperse Orange 25 (DO) and Disperse Blue 79:1 (DB) dyes, respectively. The uptake rate of dye molecules followed pseudo-second order kinetics in all cases. Recovery of dye molecules was completed best in three cycles with acetic acid for CFA and cenospheres, with Di-chloromethane for CNAC and in four cycles with non-polar solvent (chloroform) for zeolite and CNCH nanocomposite. The used adsorbents could easily be dumped into landfill with in concrete pit liming, or can also be used in brick making to minimize the environmental risk.

Keywords: cenospheres, coal fly ash, disperse dyes, response surface methodology, waste management

1. Introduction

Management of coal fly ash (CFA) at 145 coal based thermal power plants in India is a difficult task as large quantity of ash being generated. MoEF & CC had fixed the target of 100% utilization of CFA in time bound manner [1]. The average utilization percentage of CFA in various fields is about 62% only. Remaining 90 million ton of CFA is disposed into holding ponds, lagoons, landfills and slag heaps which not only requires large area of precious land for its disposal but is also one of the sources of pollution of both air and water. The utilization of CFA in 1990s was 40 million ton (3% utilization) annually and about 147 million ton (62% utilization) in 2015s [2]. The land for creating ash dyke for ash disposal facilities at thermal power plants is becoming difficult to be acquired. Thereby, CFA, if not managed well, may pose various environmental challenges.

2. Methodology

Characterization and batch adsorption study with four modified CFA adsorbents has been presented in details (**Figure 1**).

Legislative council passed a law to eliminate color from their industrial effluent before discharging dye-containing effluents into water bodies because dyes have synthetic origin and fused complex aromatic structure making them more recalcitrant to biodegradation [3, 4] (**Figure 2**).

Adsorption has evolved into one of the most effective and feasible physical processes for decolorization of textile and dyeing wastewater [5–7]. Though there is no dearth of available adsorbents like activated carbon, economic factors force consideration of alternative low cost, eco-friendly and efficient adsorbents which are either naturally available or available as waste products from other manufacturing processes and which can be utilized for the treatment of industrial effluents by the entrepreneurs of small scale industries in developing countries like India [8, 9].

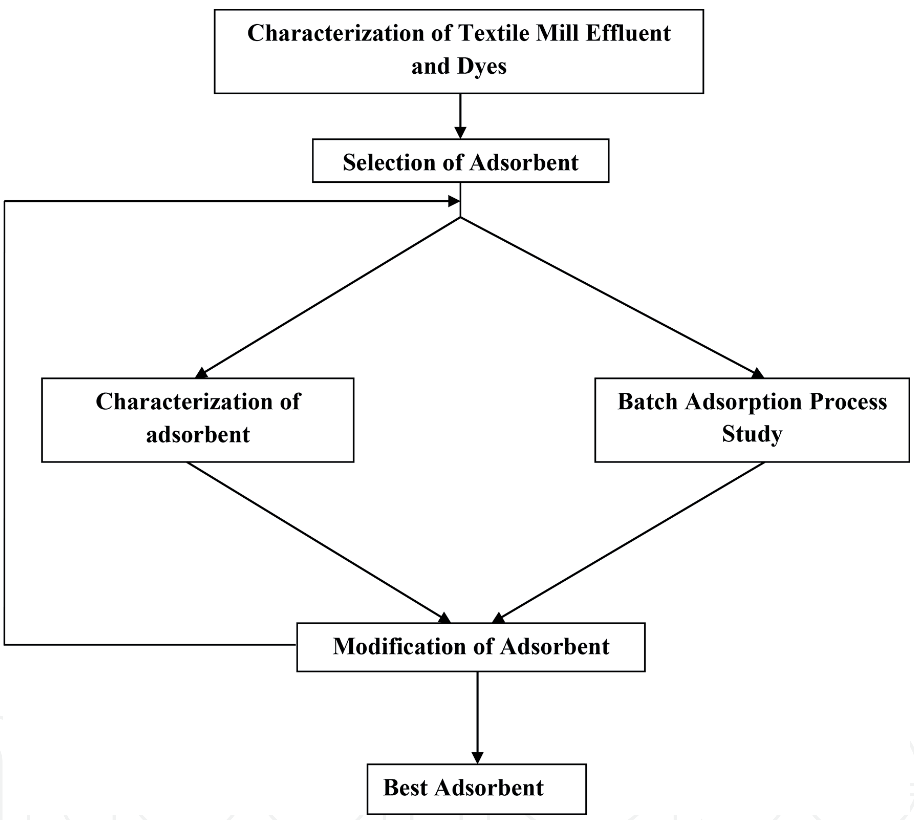

Figure 1.
General layout of study design.

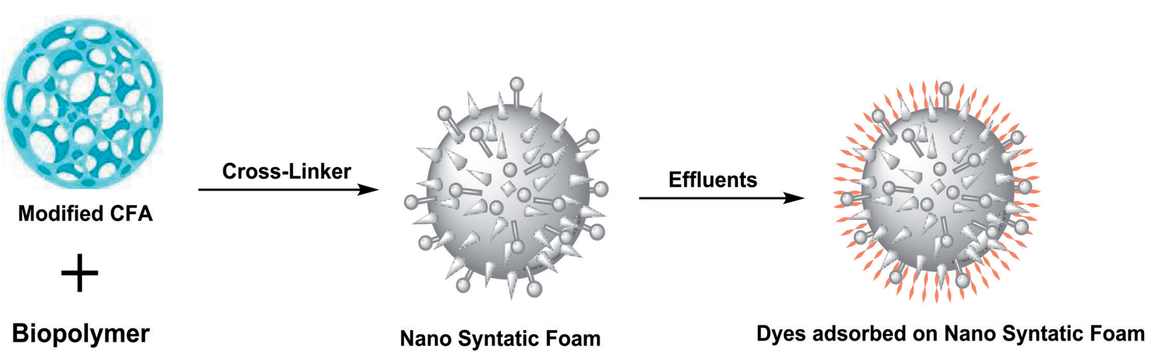

Figure 2.
Process of dye adsorption.

In this backdrop coal fly ash (CFA) has been actively pursued for its decolorizing characteristics on textile mill effluents but its relatively lower removal efficiency necessitates further modifications. Here the characterization and modification of CFA has been done to obtain the best adsorbent and the optimal conditions in which its removal efficiency for disperse dyes is maximum. To prove its efficiency, characterization of activated carbon and its comparison with our best found adsorbent have also been done [10].

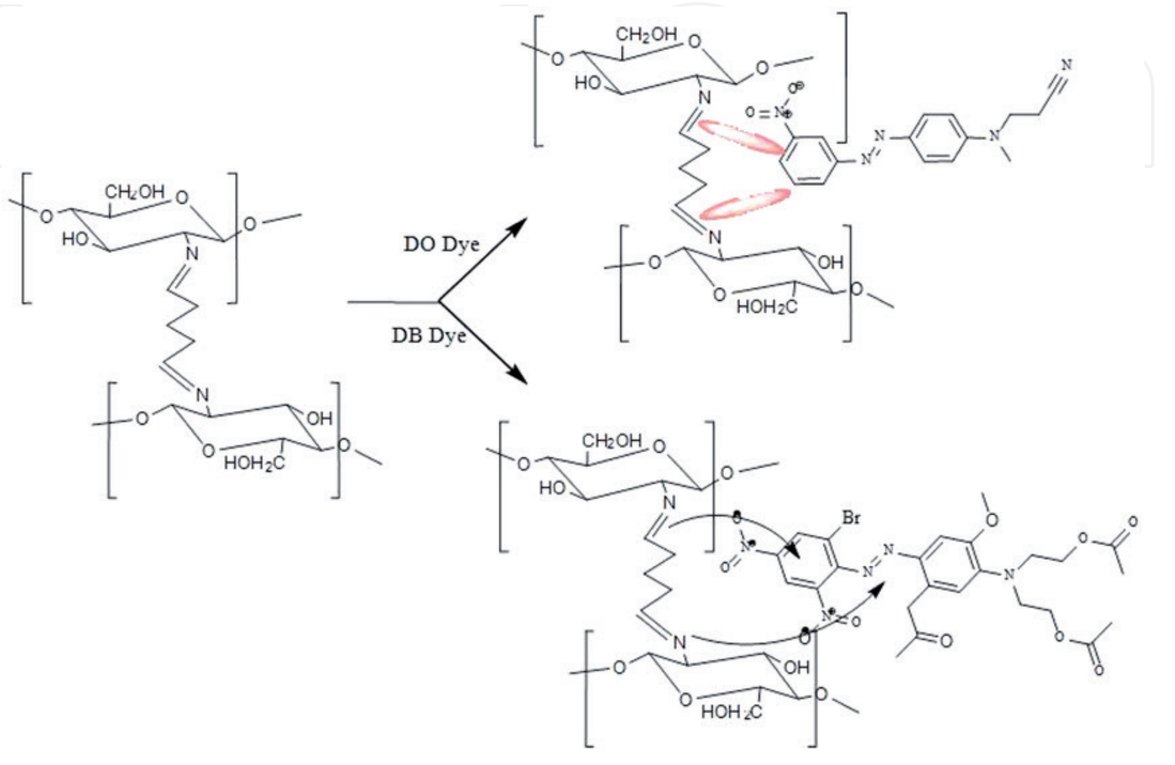

Figure 3.
Interaction between dye molecules and cross-linked natural polymer syntactic nano-foam.

3. Results and discussion

The major elemental leaching of CFA was found to be Fe > Mn > Mg. In the successive stages of research, CFA was modified and characterization studies including ATR-FTIR, SEM, EDX, XRD, TEM, CILAS and BET were conducted to analyze the adsorption potential of each modified form on the basis of its removal efficiency studied for both DO and DB dyes. From the obtained results it could be concluded that CFA has the potential to adsorb Disperse Orange 25 (DO) and Disperse Blue 79:1 (DB) dyes with 75 and 71% removal efficiency at optimized conditions and this percentage removal increased with each modification [81 and 78% in case of cenospheres, 79 and 75% for cenospheres activated carbon (CNAC) composite, 93 and 88% for zeolite, 90 and 87% for cenospheres chitosan (CNCH) nanocomposite], respectively [10–12] (**Figure 3**).

More particularly, the synthesized natural polymer syntactic nano-foam adsorbent displayed high adsorption capacities towards different class of organic dyes (hydrophobic and hydrophilic) via π-π or electrostatic interaction depending upon the nature of the dye molecules (**Table 1**).

In each case, it was found that the percentage removal of DO/DB dye had good vibes with Langmuir isotherm, which indicated saturated monolayer attachment of dye molecules onto the adsorbent with maximum capacity 1.70 and 1.55 mg/g in case of CFA, 33.33 and 32.26 mg/g in case of cenospheres, 90.91 and 83.33 mg/g

Parameters	CFA		Cenospheres		CNAC		Zeolite		CNCH		AC	
	DO	DB	DO	DB	DO	DB	DO	DB	DO	DB	DO	DB
pH	6.0		6.0		6.0		6.0		6.0		6.0	
Adsorbent dosage (g/L)	60	80	2.0	3.0	0.3 AC + 1.0 CN	0.4 AC + 1.0 CN	2.0	3.0	0.2		0.4	0.7
Adsorbate conc. (mg/L)	40		40		40		40		40		40	
Agitation speed (rpm)	140		140		140		140		200		140	
Cont. time (min)	100	120	100	120	100	120	100	120	90	120	100	120
% Removal	74	71	80	79	79	75	93	89	90	87	81	77

Table 1.
Effect of various parameters for the removal of dyes on various forms of adsorbents.

Adsorbents	DO dye (%)	DB dye (%)	Solvents
Coal fly ash (CFA)	46	39	Acetic acid
Cenospheres	48	43	Acetic acid
Cenospheres activated (CNAC) composite	59	54	Di-chloromethane
Zeolite	46	41	Chloroform
Cenospheres chitosan (CNCH) nanocomposite	47	41	Chloroform
Activated carbon	48	41	Acetic acid

Table 2.
Recovery and reusability of various adsorbents.

in case of CNAC, 125.00 and 109.80 mg/g in case of zeolite and 500.40 and 500.00 mg/g in case of CNCH nanocomposite for DO/DB dyes, respectively. The adsorption of dye molecules followed pseudo-second order kinetics in all cases. Thermodynamic study showed that process of adsorption is exothermic in nature. Recovery of dyes was completed best in three cycles with acetic acid for CFA and cenospheres, with Di-chloromethane for CNAC and in four cycles with non-polar solvent (chloroform) for zeolite and CNCH nanocomposite (**Table 2**).

After completing the analysis on the removal efficiency of each modified form of CFA, in the next stage of this work, optimization studies were done. The batch optimization process focused on effect of operating variables, such as contact time, pH, agitation speed, adsorbent dose and dye concentration using RSM with BBD. Furthermore, interactions among various parameters were investigated by applying RSM. In case of zeolite, related R^2 values of 0.9102 and 0.9038 were obtained for DO and DB dyes respectively. Optimum results indicated that 119 min of contact time was required to achieve 96% of DO dye removal at zeolite dose 0.67 g/L, dye concentration of 38 mg/L and shaking speed of 158 rpm at pH 6.10. Whereas, 95.23% of DB dye removal was found at contact time of 122 min, adsorbent dose of 1.05 g/L, dye concentration of 26.72 mg/L, agitation speed of 145 rpm and pH of 5.68. Regression modeling and ANOVA showed contact time, adsorbent dose, dye concentration, agitation speed and pH have values of 'Prob. >F'< 0.0500, which indicated that model terms were significant for adsorption of the dyes. For CNCH nanocomposites, F-values 19.91 and 19.26 for DO and DB dyes have a low probability value (Prob. >F < 0.0001), which indicate model terms are symbolic. The high R^2 value for DO (0.9409) and DB (0.9391) also showed significance of applied model. The maximum percentage removal of dyes was found to be 97.30% (DO) and 94.22% (DB). From the optimization studies, it could safely be concluded that both zeolite and CNCH nanocomposite had high potential as an efficient, eco-friendly and economic adsorbent for dye removal from aqueous solutions.

4. Conclusion

Comparing the results of the characterization and optimization studies, it could be concluded that CNCH nanocomposite was a better adsorbent than all the other modified and native form of CFA. To validate the result, CNCH nanocomposite was compared with the most widely used commercial adsorbent i.e., activated carbon. Results concluded that adsorption capacity of our best found adsorbent was more than two times of activated carbon. To further vindicate the claim that CNCH nanocomposite had high potential as an efficient, eco-friendly and economic adsorbent, it was used for the color removal from textile mill effluent. The adsorbent showed excellent removal efficiency and it was found that physico-chemical parameters also reduced after treatment of effluent. The effect of pH revealed that all the adsorbents produced good results at pH 6 implying that there was no requirement of any special acidic or basic chemical for dye removal. This pH 6 also falls within the limit of pH 5.5–9.0, i.e., industrial effluent discharge limit into the inland surface water as mandated by CPCB. Results also suggest that above CFA based adsorbents could be suitably used as alternative and effective resource materials as compared to the expensive commercial adsorbents for the removal of DO and DB dyes from colored effluents. The used adsorbents could easily be dumped into landfill with liming, in concrete pits or can also be used in brick making to minimize the environmental risk. The present work is also a forward step in reducing the pollution load by utilization of waste products in an eco-friendly manner to effectuate the goal of Agenda 21 and the Rio Declaration on Environment and Development.

Acknowledgements

The first author is highly grateful to Ms. Vibhuti Mishra for her valuable suggestions.

Conflict of interest

On behalf of all authors, the corresponding author states that there is no conflict of interest.

Author details

Markandeya[1*], S.P. Shukla[2,3] and Devendra Mohan[1]

1 Department of Civil Engineering, Indian Institute of Technology-BHU, Varanasi, India

2 Department of Civil Engineering, Institute of Engineering and Technology, Lucknow, India

3 Rajkiya Engineering College, Banda, India

*Address all correspondence to: mktiwariiet@gmail.com; markandeya.civ@iitbhu.ac.in

References

[1] Government of India, Ministry of Environment and Forests. Fly Ash Notification. 2009. Available from: http://dste.puducherry.gov.in/Flyash_notification2009.pdf

[2] Central Electricity Authority of India. Annual Report on Fly Ash Utilization. 2015. Available from: cea.nic.in/reports/others/thermal/tcd/flyash_final_1415.pdf

[3] Dhiman N, Markandeya, Fatima F, Roy S, Rout PK, Saxena PN, et al. Predictive modeling and validation of arsenite removal by one pot synthesized bioceramic buttressed manganese doped iron oxide nanoplatform. RSC: Advances. 2017;**7**:32866-32876

[4] Dhiman N, Markandeya, Singh A, Verma NK, Ajaria N, Patnaik S. Statistical optimization and artificial neural network modeling for acridine orange dye degradation using in-situ synthesized polymer capped ZnO nanoparticles. Journal of Colloid and Interface Science. 2017;**493**:295-306

[5] Markandeya, Dhiman N, Shukla SP, Kisku GC. Statistical optimization of process parameters for removal of dyes from wastewater on chitosan cenospheres nanocomposite using response surface methodology. Journal of Cleaner Production. 2017;**149**:597-606

[6] Markandeya, Shukla SP, Dhiman N. Characterization and adsorption of disperse dyes from wastewater onto cenospheres activated carbon composites. Environmental Earth Sciences. 2017;**76**:702-714

[7] Shukla SP, Sonam, Markandeya, Mohan D, Pandey G. Removal of fluoride from aqueous solution using *Psidium guajava* leaves. Desalination and Water Treatment. 2017;**62**:418-425

[8] Markandeya, Dhiman N, Shukla SP, Mohan D, Kisku GC, Patnaik S. Comprehensive remediation study of disperse dyes containing wastewater by using environmental benign, low cost cenospheres nanosyntactic foam. Journal of Cleaner Production. 2018;**182**:206-216

[9] Tiwari M, Shukla SP, Mohan D, Bhargava DS, Kisku GC. Modified cenospheres as an adsorbent for the removal of disperse dyes. Advances in Environmental Chemistry. 2015;**2015**:1-8

[10] Kisku GC, Markandeya, Shukla SP, Singh DS, Murthy RC. Characterization and adsorptive capacity of coal fly ash from aqueous solutions of disperse blue and disperse orange dyes. Environmental Earth Sciences. 2015;**74**(2):1125-1135

[11] Markandeya, Shukla SP, Dhiman N, Mohan D, Kisku GC, Roy S. An efficient removal of disperse dye from wastewater using zeolite synthesized from cenospheres. Journal of Hazardous, Toxic, and Radioactive Waste. 2017;**21**(4):04017017

[12] Markandeya, Shukla SP, Mohan D. Toxicity of disperse dyes and its removal from wastewater using various adsorbents: A review. Research Journal of Environmental Toxicology. 2017;**9**:01-18